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<b>(21) International Application Number:</b> PCT/AU91/00076 <b>(22) International Filing Date:</b> 6 March 1991 (06.03.91) <b>(30) Priority data:</b> PJ 8972 6 March 1990 (06.03.90) AU <b>(71)(72) Applicant and Inventor:</b> TATE, David [AU/AU]; Pleasant View, Hillston Highway, Hillston, NSW 2675 (AU). <b>(74) Agent:</b> GORDON, Glen, Howard; Arthur S. Cave & Co., Level 10, 10 Barrack Street, Sydney, NSW 2000 (AU). <b>(81) Designated States:</b> AT, AT (European patent), AU, BB, BE (European patent), BF (OAPI patent), BG, BJ (OAPI patent), BR, CA, CF (OAPI patent), CG (OAPI patent), CH, CH (European patent), CM (OAPI patent), DE, DE (European patent), DK, DK (European patent), ES, ES (European patent), FI, FR (European patent), GA (OAPI patent), GB, GB (European patent), GR (European patent), HU, IT (European patent), JP, KP, KR, LK, LU, LU (European patent), MC, MG, ML (OAPI patent), MR (OAPI patent), MW, NL, NL (European patent), NO, PL, RO, SD, SE, SE (European patent), SN (OAPI patent), SU, TD (OAPI patent), TG (OAPI patent), US.		<b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> FUNGICIDAL COMPOSITIONS FOR APPLICATION TO PLANTS  <b>(57) Abstract</b>  A fungicidal composition for application to plants comprising a fungistat, or compound that acts as a fungicide, in a mixture with another substance that produces a positive chemotactic response from myco-pathogens. Compounds which produce a positive chemotaxis response from a fungi are for example organic acids such as citric or malic acids, amino acids such as glutamic or aspartic acids, fatty acids such as oleic or palmitic acids, or aldehyde derivatives of these acids or saccharides and polysaccharides such as sucrose, galactose or maltose, or pectic or glycoside derivatives of the sugars. The preferred fungicide is a copper based fungicide, preferably a salt of a copper (II) complex, most preferably the cupric tetra ammine, $\text{Cu}(\text{NH}_3)_4^{2+}$ complex. A method of combatting fungal infections in plants is also described.		

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## FUNGICIDAL COMPOSITIONS FOR APPLICATION TO PLANTS

Technical Field

The invention concerns a fungicidal composition for application to plants. The fungicidal composition can be a known fungicide in admixture with another substance that produces a positive chemotactic response from the myco-pathogen. The preferred fungicide is a copper-based fungicide. The preferred fungicide is a salt of a copper (II) complex, the cupric tetra ammine,  $\text{Cu}(\text{NH}_3)_4^{2+}$  complex. In addition,  $\text{Cu}(\text{NH}_3)_4^{2+}$  is a new fungistat and can be used as a fungicide, either with or without the chemotactic ingredient. The ammonia ligands of the copper (II) complex also have positive chemotaxis. The invention also relates to a method of combatting fungal and other myco-pathogenic infections in plants.

Background Art

Copper based fungicides presently in use in agriculture, derive their fungicidal activity from copper's broad anti-microbial spectrum of activity. Typically, known copper based fungicides include formulations of the following materials: copper sulphate and water ( $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ ), copper sulphate and calcium hydroxide and water ( $\text{CuSO}_4 \cdot \text{Ca}(\text{OH})_2 \cdot \text{H}_2\text{O}$ ), copper sulphate and sodium hydroxide and water ( $\text{CuSO}_4 \cdot \text{NaOH} \cdot \text{H}_2\text{O}$ ), cupric hydroxide ( $\text{Cu}(\text{OH})_2$ ), and copper oxychloride ( $\text{CuOCl}$ ), for example.

Most of these known copper based fungicides have their fungicidal activity inhibited by the close association or direct bonding of ions of elements that reduce the number of free active sites on the copper (II) ion. Moreover, most of the known copper based fungicides can form insoluble compounds, on contact with other substances in the environment, resulting in precipitation of the copper compound. There are difficulties and increased costs arising from their application, and especially with unwanted post

harvest residues containing copper.

A major difficulty with the known art is the presence of sodium or chlorine or other anions such as hydroxide or sulphate within the copper based fungicides that restrict microbial (i.e. fungal) activity. The presence of these anionic molecules, being largely of a negatively chemotaxic nature, results in a biochemical inhibition of the surface microflora on the plant surface. The effect of this is to reduce the effectiveness of the applied copper as the resting inoculum is forced to hibernate through the unfavourable conditions.

A further problem is caused by the reduced level of Cu(II) activity after application to the plant surface, and the disrupted biological signals on the plant. The application of the fungicide at a level necessary to inhibit the inoculum can subsequently cause phytotoxicity symptoms in many crops. Thus, the use of copper based fungicides is limited and even prevented, in some crops. Similar problems occur with other types of fungicides.

No copper based or other types of fungicides are specifically designed to positively alter plant surface conditions as a means of maximising the eradicator effect of the copper (II) ions, or other active ingredients that are present. Previously, no attempt has been made to control the fungal activity by encouraging spore germination in the presence of a fungistat.

Thus, there is a need for an improved copper based or other formulation of a fungicide which would additionally allow incorporation of substances to increase fungal activity, specifically by encouraging fungal spore germination and hence enabling greater control of the infection.

#### Disclosure of Invention

The present invention provides a fungicidal composition comprising a fungicide such as a copper (II) based fungicide, together with one or more substances that produce a positive myco-chemotaxic response from the target pathogen. Some examples of these types of materials are:

organic acids such as citric or malic acids; amino acids such as glutamic or aspartic acids; fatty acids such as oleic or palmitic acids and/or aldehyde derivatives of these acids. Also saccharides or polysaccharides can be used, such as sucrose or galactose, or pectic, or glycoside derivatives, or polymeric materials that have components composed of saccharides. Other such substances, or combinations of these and other materials can be used, and can be changed according to the crop and type of infection.

The preferred fungicide is a copper (II) based fungicide, and in particular, a salt of a copper (II) complex, the ligands having positive chemotaxic responses from the target pathogens. The preferred ligand is ammonia, although other ligands, particularly those being derivatives of ammonia, or having amine groups, are preferred. The invention also comprises the use of these copper complexes alone as fungicides, and fungicidal compositions of this sort.

The fungicide of the present invention comprises known fungicides, particularly copper-based, and most particularly the cupric tetra ammine complex, and their salts, in combination with specific substances which can be used as food sources in the process of respiration. The specific molecules are preferably organic acids (e.g. citric acid, and malic acid); amino acids (e.g. glutamic, aspartic acids); fatty acids (e.g. oleic, palmitic acids), or derivatives of these acids, particularly the aldehyde derivatives; saccharides or polysaccharides (e.g. dextrose, maltose galactose, glucose, etc); or combinations of organic acids and saccharides (e.g. citric acid and fructose) or the pectic or glycoside derivatives of these sugars; the choice of which, depends upon the crop and type of fungus.

If carbohydrates are available, most fungi can synthesise their own proteins by utilising inorganic sources of nitrogen. The increased incidence of plant diseases associated with high nitrogen fertiliser usage and the micro-flora's essential requirement for nitrogen for development and reproduction, indicate the suitability of a nitrogenous ligand for the copper (II) ion or for the other

active ingredients possible in the invention.

Chemotaxis, also known as chemotropism, describes the attraction of living organisms to chemical stimuli, whereby the cells are attracted, if there is positive chemotaxis, or otherwise repelled, if there is negative chemotaxis. Chemotactic substances are often acids, alkalis or other substances that exhibit chemical activity to living protoplasm.

For example, the copper (II) ion is negatively myco-chemotactic. Therefore, to encourage the pathogenic inoculum to come in contact with the applied fungicide composition, the association of the copper (II) ions with nitrogen containing substances is ideal, as one solution to this problem.

Nitrogen containing compounds and/or acids such as "fruit" acids, and sugars, and their derivatives, are used as sources of cellular materials and energy. These are metabolic stimulants encouraging the microflora to germinate and forage. The amount of microbial activity will also depend on temperature and moisture at the time of application.

When preparing the fungicide and during its application, the invention, in a preferred form utilises a soluble ligand, especially ammonia, for the copper (II) ions in preference to copper hexahydrate  $(\text{Cu}(\text{H}_2\text{O})_6)^{2+}$  which is the previously known copper fungistat. Upon application, the four ammonia ligands are gradually substituted by water, thereby allowing  $\text{Cu}^{2+}$  ions to be liberated within solution, on the plant surface.

Other ligands can be used to bond to the copper ions, which are gradually liberated and substituted with water. These ligands should have positive chemotaxis. The ligands can be monodentate, like ammonia, or polydentate, like bipy (2,2-bipyridine). Some examples of such ligands are ammonia, ethylenediamine, bipy, triethylenetetramine, and derivatives thereof. Nitrogen containing ligands are preferred, that bond to the copper via their nitrogen atom(s).

In addition, one aspect of the invention includes the inclusion of further positive chemotactic substances to the

formulation. For example, organic acids, and in particular, citric acid, or malic acid, can be used. Citric acid is well known to keep copper from forming hydroxide complexes in basic solutions. It is unlikely that copper citrate is formed in such conditions, since large amounts of energy are required to form copper citrate, and therefore it is believed that hydrolysed copper remains in solution as  $\text{Cu}(\text{H}_2\text{O})_6^{++}$ .

The invention utilises the bond between  $\text{Cu}^{++}$  ions and  $\text{NH}_3$  to form the square planar cupric tetra ammine molecule  $\text{Cu}(\text{NH}_3)_4^{2+}$ . The complex may be hydrated to form  $\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2^{2+}$  ions. The complex is similar to that formed by free copper (II) in water. Salts of copper (II) tetra ammine such as  $\text{Cu}(\text{NH}_3)_4(\text{NO}_3)_2$ ,  $\text{Cu}(\text{NH}_3)_4\text{SO}_4$ , and  $\text{Cu}(\text{NH}_3)_4(\text{OH})_2$  can be used in the compositions of the invention.

The ligands such as tetra ammine component of the  $\text{Cu}(\text{NH}_3)_4^{2+}$  complex ideally hydrolyse or "weather" within a sufficient period of time to provide micro-pathogens with their nutritional nitrogen needs, also making available active copper (II) ions.

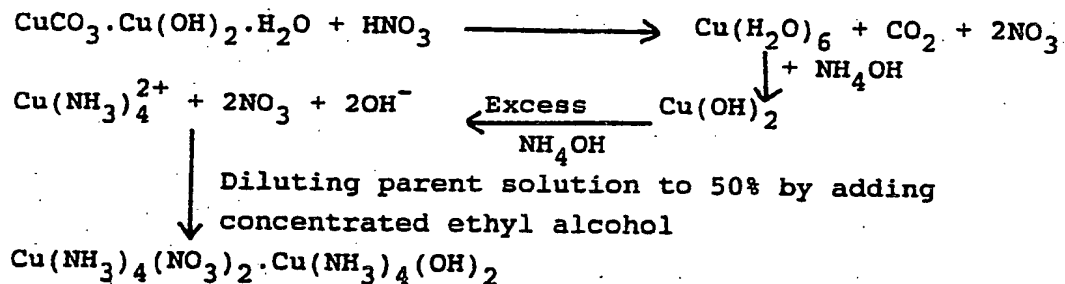
Further, nitrogen containing molecules within the plant tissues and upon the plant surface are used by parasitic organisms for their own functions. For this reason it is believed that the tetra ammine complex does not discourage parasitic organisms from germinating in the presence of  $\text{Cu}(\text{II})$  ions.

The  $\text{NH}_3$  or other chemotactic ligand present is also a useful source of plant foliar nitrogen nutrition.

The  $\text{Cu}(\text{NH}_3)_4^{2+}$  is a new fungicidally effective substance, and therefore the invention is also directed to compositions containing the complex, together with a suitable anion, and other diluents, carriers or additives usual in fungicidal compositions. In addition, this ingredient can be combined with a substance as described previously that produces a positive chemotactic response from the target fungi. The compositions of the invention can be applied to the plants in any conventional manner. For example, spraying

or dusting are suitable such methods.

The preparation of cupric tetra amine compounds of the invention can be carried according to the following reaction scheme.



Thus the improved fungicides of the present invention overcome difficulties of conventional, especially, copper based, fungicides by directing copper (II) ions to the target fungal infection, in a medium of the growth substances which are used by the microbe, and also preferably supplying nutrient nitrogen in the form of ammonia that is bound to the copper, for example.

In this way the fungicide formulations of the present invention, by incorporating microbial foodstuffs, specific compounds used as food sources for respiration as discussed above, will control fungal infections by encouraging spore germination and foraging.

A further embodiment of the invention is the inclusion of ingredients that prevent the formation of insoluble copper compounds at the time of application, on the plant surface, while excluding those materials likely to interfere with the activity of copper (II) ions. Thus the copper (II) ion remains more mycologically active.

The formulations of the invention are generally soluble when they are applied, and later when they are on plant surfaces. By remaining soluble they avoid problems such as blocking equipment application and not precipitating in spraying devices, for instance. Post harvest residue problems common to the known art are also eliminated, by using the formulations of the invention.

#### MODES FOR CARRYING OUT THE INVENTION

The invention is now described with reference to examples.



Example 1

(a) A formulation of the invention is prepared as follows:

$\text{Cu}(\text{HN}_3)_4(\text{NO}_3)_2$ [Cupric tetra ammine nitrate]	256 gm
$\text{C}_6\text{H}_8\text{O}_7$ Citric acid (crystalline)	144 gm
$\text{C}_6\text{H}_{12}\text{O}_6$ Dextrose (crystalline)	<u>60 gm</u>
The total amount of the formulation produced is	460 gm

To the formulation was added 100 litres of water and a surfactant. This solution is then sprayed on to lemon scab (Elsinoe faucettii) susceptible lemon foliage and fruitlets to the point of run-off, every ten days, while both weather, and, crop conditions, are favourable to infection. The present invention has the advantage that only 64 gram of elemental copper is applied as opposed to 100-150 grams of copper per 100 litres of  $\text{H}_2\text{O}$  in the known technology.

(b) A second formulation was prepared as described in part (a) above, as follows:

$\text{Cu}(\text{HN}_3)_4(\text{NO}_3)_2$ [Cupric tetra ammine nitrate]	250 gm
$\text{C}_6\text{H}_8\text{O}_7$ Citric acid (crystalline)	60 gm
$\text{C}_6\text{H}_{12}\text{O}_6$ Dextrose (crystalline)	<u>140 gm</u>
The total amount of the formulation produced is	450 gm

Example 2

(a) A further formulation was prepared, suitable for stone fruit whilst in foliage:

$\text{Cu}(\text{NH}_3)_4\text{SO}_4 \cdot \text{Cu}(\text{NH}_3)_4(\text{OH})_2$	133 gm
Citric acid	87 gm
Malic acid	10 gm
Maltose	<u>40 gm</u>
Fungicide per 100 L $\text{H}_2\text{O}$	270 gm

The equivalent of 43 gm of elemental copper is applied to the control shot hole, rust and brown rot, between growth flushes in October and again in December.

(b) A second formulation was prepared in accordance with the method described in part (a), as follows:

$\text{Cu}(\text{NH}_3)_4\text{SO}_4 \cdot \text{Cu}(\text{NH}_3)_4(\text{OH})_2$	130 gm
Citric acid	20 gm
Malic acid	50 gm
Galactose	<u>250 gm</u>
Fungicide per 100 L $\text{H}_2\text{O}$	450 gm

Example 3

A further formulation of the invention suitable for control of citrus melanose disease in oranges is prepared as follows:

200 grams of  $\text{Cu}(\text{NH}_3)_4 \cdot (\text{NO}_3)_2$  [cupric tetra ammine nitrate] is added to 100 L of  $\text{H}_2\text{O}$  together with an adjuvant and the mixture then applied to oranges with citrus melanose disease.

Example 4

A further formulation of the invention suitable for control of apple scab Venturia-inaequalis in apples in leaf is prepared as follows:

200 grams of  $\text{Cu}(\text{NH}_3)_4 \cdot (\text{NO}_3)_2$  [cupric tetra ammine nitrate] together with 114 grams of  $\text{H}_2\text{PO}_3$  (phosphoric acid) per 100 L of  $\text{H}_2\text{O}$ , the mixture being applied to apples in leaf for the control of apple scab Venturia-inaequalis.

Example 5

The formulations for the production of a cupric tetra ammine can be prepared, for example, by the following reaction scheme.

Copper carbonate is dissolved in dilute nitric acid and then ammonia is added until cupric hydroxide precipitates. The continued addition of ammonia results in the dissolution of the cupric hydroxide to produce cupric tetra ammine in solution.

The addition of 50% by volume of ethyl alcohol to the solution and evaporation, yields, a blue crystalline substance of  $\text{Cu}(\text{NH}_3)_4(\text{NO}_3)_2$ , in the nitrate form. An amount of  $\text{Cu}(\text{NH}_3)_4(\text{OH})_2$  may also be present.

Example 6

To understand the invention further an investigation of the fungal disease wheat rust Puccinia Striaformis was conducted.

The host plant, wheat Triticum aestivum stores its soluble carbohydrates in its stem internodes as fructans. Invasion by the P. striaformis fungi utilises these stored carbohydrates for fungal growth and reproduction (see

"Fructans polymerised and depolymerised in the internodes of winter wheat", Blacklow, Darbyshire and Phelong, Plant Science Letters Vol.36 1984 p213-218.) These researchers found that the stem internodes of wheat stored fructose units as fructans polymerised to a Degree of Polymerisation (D.P.) of 9. Fructans of a D.P. equal to or greater than 5 are stored at twice the concentration of those of a D.P. of 3 and 4. These researchers found that at grain filling the fructans are depolymerised to fructose and the sugars are utilised in the grain development.

The aeciospore of the P. striaformis germinates freely in moisture on the host plants surface. The growth of a pre-haustoria by most spores occurs at night and a patterned motile development of this pre-haustoria towards a stomate occurs. This motile development resembles an indirect migration to the stomate and is either a tactile response or a response to CO<sub>2</sub> gradients from stomatal emissions. Once at the stomate the fungi gathers itself above the unopened stomate as an appressoria, and at first light as the stomate opens the pathogen enters and forms within a sub-stomatal vesicle. Penetration of the parenchyma and invasion takes place.

The new fungicidal compositions of the invention aim to destroy the germinating aeciospore and motile pre-haustoria prior to the development of the appressoria. The means involves the application of the polymerised carbohydrates to the surface of the plant with an initially disguised fungistat. The effects on the pathogen are four fold. Firstly, the applied polymers effectively extend the surface solution producing a net-like polymer structure. This polymer structure applied to the plant surface inhibits the tactile development to the stomate by the motile pre-haustoria.

Secondly, in response to the polymerised carbohydrates (either within or externally); the pathogen employs beta amylase and then maltose enzymes from its enzyme resource. Mucolytic or hemicellulase enzymes necessary for host penetration from the sub-stomatal vesicle may well be

compromised. Thirdly, the excipient quality of the sugar polymers aids in the introduction of the fungistat, and finally, the externally induced enzyme activity from the pre-haustoria in the plant surface solution and the  $\text{Cu}^{2+}$  ions liberated from the  $\text{Cu}(\text{NH}_3)_4^{2+}$  molecule disrupts disease progression.

A small quantity of citric acid (0.03%) is included to prevent reduction of the  $\text{Cu}^{2+}$  ion by the reducing sugars that make up the polymers. 30gm  $\text{C}_6\text{H}_8\text{O}_7$ /100 L  $\text{H}_2\text{O}$ . A 0.33%  $\text{Cu}^{2+}$  concentration is applied with 118gm  $\text{Cu}(\text{NH}_3)_4\text{SO}_4$ /100 L  $\text{H}_2\text{O}$ .

The formulation, therefore to be applied per 100 L of  $\text{H}_2\text{O}$  is as follows:

Cupric tetra ammine sulphate	$\text{Cu}(\text{NH}_3)_4\text{SO}_4$	118gm
Citric Acid	$\text{C}_6\text{H}_8\text{O}_7$	30gm
L-Glutamic Acid	$\text{C}_5\text{H}_7\text{O}_4(\text{NH}_2)$	20gm
L-Aspartic Acid	$\text{C}_4\text{H}_5\text{O}_4(\text{NH}_2)$	16gm
DL-Alanine	$\text{C}_3\text{H}_5\text{O}_2(\text{NH}_2)$	12gm
Palmitic Acid	$\text{C}_{16}\text{H}_{32}\text{O}_2$	60gm
Dextrin (D.P. 4 to 9)	$\text{C}_6\text{H}_{12}\text{O}_6$	200gm

In general, preferential stimulants other than the carbohydrate polymers can be chosen from other materials found within the host or known to have a desired effect upon the pathogen. They include fatty acids and of these palmitic acid is the most significant, ( $\text{C}_{16}\text{H}_{32}\text{O}_2$ ). Amino acids, although in minor quantities, are preferred stimulants. Of these glutamic and aspartic acids and alanine are significant though others can also be beneficial.

Fructans can be sourced as inulins and applied at 0.15% or 150gms/100 litre of  $\text{H}_2\text{O}$ . Alternatively dextrans which are chemically similar to fructans and considerably cheaper can be used. A 90% soluble dextrin of a D.P. 4 to 9 containing not more than 5% reducing sugar and less than 1% alcohol solubles can be applied at 0.2% of solution 200gm/100 L  $\text{H}_2\text{O}$ .

The inclusion of a crop spray oil applied in accordance with manufacturers recommendations will improve coverage.

EXAMPLE 7

A further investigation was conducted of Citrus Brown Rot: Causal organism Phytophthora Citrophthora. A formulation was prepared with respect to overcoming the introduction of P. Citrophthora zoospores to the vicinity of citrus host tissues:

<u>Components</u>	<u>Per 100L H<sub>2</sub>O</u>
Cu(NH <sub>3</sub> ) <sub>4</sub> SO <sub>4</sub>	115gm
Citric Acid (Anhydrous)	30gm
DL-Malic Acid (Free Acid)	90gm
Sucrose (Crystalline)	210gm
D-Fructose (Crystalline)	250gm
D+Glucose (Anhydrous)	180gm
L-Aspartic (Cryst. Free Acid)	16.5gm
L-Glutamic (Cryst. Free Acid)	18.5gm
Hesperidin	40gm
Rutin	10gm

The application of such a large number of constituents in amounts consistent with those found within the citrus host is aimed at combatting a broad range of fungal infections, by creating a plant surface solution which is chemotactically confusing to any pathogen..

Crop spray oil should also be included when applying the formulation.

EXAMPLE 8

A formulation was prepared for treatment of Peach Brown Rot, causal organism Monilinia Fructicola. The formulation of the invention was prepared as follows:

<u>Components</u>	<u>Per 100L H<sub>2</sub>O</u>
Na poly pectate	400gm
Cu(NH <sub>3</sub> ) <sub>4</sub> SO <sub>4</sub>	90gm
DL-Malic Acid	50gm
Sucrose	120gm
Fructose	40gm
L-Aspartic Acid	20gm

This formulation was directed to preferential stimulation of M. fructicola. The waxy cuticle of the peach is hydrophillic in nature and the application of 250ml of crop spray oil per 100 L H<sub>2</sub>O will improve coverage.

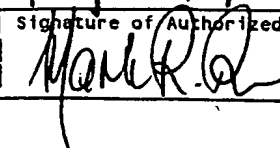
The claims:

1. A fungicidal composition for application to plants which comprises a fungicide together with at least one substance that produces a positive chemotactic response from myco-pathogens.
2. The fungicidal composition of claim 1 wherein the chemotactic substance is selected from: organic acids, amino acids, fatty acids, saccharides, polysaccharides, and salts and derivatives thereof.
3. The fungicidal composition of claim 2 wherein the chemotactic substance is selected from: citric acid, malic acid, glutamic acid, aspartic acid, oleic acid, palmitic acid, the aldehyde derivatives of said acids, sugars including sucrose, fructose, or galactose, or the pectic, glycoside, or polymeric derivatives of the said sugars.
4. The fungicidal composition of claim 1 which also contains one or more fungicidally effective carriers, diluents, surfactants or other conventional additives.
5. The fungicidal composition of claim 1 wherein the fungicide is a copper-based fungicide.
6. The fungicidal composition of claim 5 wherein the fungicide is a salt and/or complex of copper (II).
7. The fungicidal composition of claim 6 wherein the fungicide is a copper (II) complex having one or more mono- or polydentate ligands, the ligands producing a positive chemotactic response from myco-pathogens, or a salt thereof.
8. The fungicidal composition of claim 7 wherein the copper (II) complex is a salt of  $\text{Cu}(\text{NH}_3)_4^{2+}$ .
9. A fungicidal composition comprising, as a fungicide, a copper (II) complex having one or more mono- or polydentate ligands, the ligands producing a positive chemotactic response from myco-pathogens, or a salt thereof, together with a fungicidally suitable carrier or diluent.

10. The fungicidal composition of claim 9 wherein the fungicide is a salt of  $\text{Cu}(\text{NH}_3)_4^{2+}$ .
11. A method of treating or preventing myco-pathogenic attack on a plant which comprises applying to the plant an effective amount of a fungicide and at least one substance that produces a positive chemotactic response from myco-pathogens.
12. The method of claim 11 wherein the chemotactic substance is selected from: organic acids, amino acids, fatty acids, saccharides, polysaccharides, and salts and derivatives thereof.
13. The method of claim 12 wherein the chemotactic substance is selected from: citric acid, malic acid, glutamic acid, aspartic acid, oleic acid, palmitic acid, the aldehyde derivatives of said acids, sugars including sucrose, fructose, or galactose, the pectic, glycoside, or polymeric derivatives of the said sugars.
14. The method of claim 11 wherein the fungicide is a copper-based fungicide.
15. The method of claim 14 wherein the fungicide is a salt and/or complex of copper (II).
16. The method of claim 15 wherein the fungicide is a copper (II) complex having one or more mono- or polydentate ligands, the ligands producing a positive chemotactic response from mycopathogens, or a salt thereof.
17. The method of claim 16 wherein wherein the copper (II) complex is a salt of  $\text{Cu}(\text{NH}_3)_4^{2+}$ .
18. A method of treating or preventing myco-pathogenic attack on a plant which comprises applying to the plant an effective amount of a copper (II) complex having one or more mono- or polydentate ligands, the ligands producing a positive chemotactic response from myco-pathogens, or a salt thereof.
19. The method of claim 18 wherein a salt of  $\text{Cu}(\text{NH}_3)_4^{2+}$  is applied to the plant.

# INTERNATIONAL SEARCH REPORT

International Application No. **PCT/AU 91/00076**

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (if several classification symbols apply, indicate all) 6				
According to International Patent Classification (IPC) or to both National Classification and IPC				
Int. Cl. <sup>5</sup> A01N 59/20, 35/00, 37/02, 37/06, 37/36, 37/44, 55/02				
<b>II. FIELDS SEARCHED</b>				
Minimum Documentation Searched 7				
Classification System	Classification Symbols			
IPC	WPAT and USPA Derwent Databases. A01N and Keywords: "CHEMOTA:", "COPPER", "CUPRIC", "CUPROUS"			
Documentation Searched other than Minimum Documentation to the extent that such documents are included in the fields searched 8				
Chemical Abstracts : Keywords : "FUNGICIDE", "CHEMOTA:", "COPPER", "CUPRIC", "CUPROUS" AU : IPC as above				
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT</b> 9				
Category*	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages 12	Relevant to Claim No 13		
X	Derwent Abstract Accession no. 88-089171/33, Class P34, JP,A, 63-041408 (NIPPON ZEON KK) 22 February 1988 (22.02.88)	(1,2,5,6,11,12, 14,15)		
X	Derwent Abstract Accession no. 87-217091/31, Class P15, JP,A, 62-142559 (SHOKO KAGAKU KENKYU) 25 June 1987 (25.06.87)	(1,2,5,6,11,12, 14,15)		
X	Patents Abstracts of Japan, C-409, page 13, JP,A, 61-233606 (RIKAGAKU KENKYUSHO) 17 October 1986 (17.10.86)	(1,2,5,6,11,12 14,15)		
X	Patents Abstracts of Japan, C-201, page 8, JP,A, 58-162508 (TEIJIN K.K.) 27 September 1983 (27.09.83)	(1-3,5-8,11-15)		
X	Patents Abstracts of Japan, C-134, page 154, JP,A, 57-131708 (RIKAGAKU KENKYUSHO) 14 August 1982 (14.08.82)	(1,2,5,6,11,12, 14,15)		
(continued)				
<p>* Special categories of cited documents: 10</p> <table style="width: 100%;"> <tr> <td style="width: 50%; vertical-align: top;"> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </td> <td style="width: 50%; vertical-align: top;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"G" document member of the same patent family</p> </td> </tr> </table>			<p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p>	<p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"G" document member of the same patent family</p>
<p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p>	<p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"G" document member of the same patent family</p>			
<b>IV. CERTIFICATION</b>				
Date of the Actual Completion of the International Search 20 June 1991 (20.06.91)		Date of Mailing of this International Search Report 20 June 1991 (20.06.91)		
International Searching Authority  Australian Patent Office		Signature of Authorized Officer   M. ROSS		



## FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

X	Patents Abstracts of Japan, C-78, page 3289, JP,A, 53-109910 (KAKEN KAGAKU K.K.) 26 September 1978 (26.09.78)	(1,2,5,6,11,12, 14,15)
X	GB,A, 1585967 (B P CHEMICALS LIMITED) 11 March 1978 (11.03.78)	(1,2,4-12,14-19)
X	US,A, 4590208 (HILDITCH, E.A. et al) 20 May 1986 (20.05.86)	(1,2,4,5,6,11,12, 14,15)
P,X	AU,A, 65898/90 (DR. WOLMAN GMEH) 16 May 1991 (16.05.91)	(1,2,4,5,6,11,12, 14,15)

V. ☐ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE 1

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claim numbers ..., because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claim numbers , because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claim numbers ..., because they are dependent claims and are not drafted in accordance with the second and third sentences of PCT Rule 6.4 (a):

VI. ☐ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING 2

This International Searching Authority found multiple inventions in this international application as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.
2. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:
3. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:
4. ☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

## Remark on Protest

- ☐ The additional search fees were accompanied by applicant's protest.  
☐ No protest accompanied the payment of additional search fees.

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON  
INTERNATIONAL APPLICATION NO. PCT/AU 91/00076

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report		Patent Family Members			
JP 63041408	US 4956183				
US 4590208	AU 46746/79 EP 5361 US 4374852	CA 1115461 NZ 190390	DK 1869/79 PT 69572		
AU 65898/90	DE 3937658	EP 431315			

END OF ANNEX